K$^+$-doped poly(ε-caprolactone)/siloxane biohybrid electrolytes for electrochromic devices

M. Fernandes[a], L. C. Rodrigues[b], R. A. Sá Ferreira[c], A. Gonçalves[d], E. Fortunato[d], M. M. Silva[b], M. J. Smith[b], L. D. Carlos[c], V. de Zea Bermudez[a*]

^{a} *Departamento de Química /CQ-VR, Universidade de Trás-os-Montes e Alto Douro, 5001-801 Vila Real, Portugal*

^{b} *Departamento de Química/Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal*

^{c}*Departamento de Fisica/CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal*

^{d}*CENIMAT/I3N, Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, FCT, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal*

ABSTRACT

Sol-gel derived KCF$_3$SO$_3$-doped di-urethane cross-linked poly(ε-caprolactone) (PCL(530))/siloxane ormolytes with ∞ > n ≥ 0.5 (n indicates the number of (C(=O)(CH$_2$)$_5$O) repeat units per K$^+$ ion) have been studied. Xerogel samples with n ≥ 1 are thermally stable up to 235 ºC. A minor proportion of PCL crystallites occur in some dilute-to-concentrated samples. At n ≤ 4 a crystalline PCL(530)/siloxane-KCF$_3$SO$_3$ complex with unknown stoichiometry emerges. At n ≤ 2 this complex coexists with pure salt. At temperatures higher than 40 ºC the composition which exhibits the highest ionic conductivity is n = 21. "Free" anions, weakly coordinated CF$_3$SO$_3^-$ ions, contact ion pairs and several higher ionic aggregates emerge in all the

---

* Phone: 00-351-259-350253; Fax: 00-351-259-350480; E-mail: vbermude@utad..pt

samples. The K^+ ions bond to the oxygen atoms of the carbonyl groups of the urethane and ester groups, of the PCL (530) ether chain and of the triflate ions at all salt concentrations. The ormolytes were successfully used in the production of prototype electrochromic devices (ECDs) that exhibit low switching time and good open circuit memory.. The ECD incorporating the ormolyte with n = 21 displays an average transmittance in the visible region of ca. 55 % in the colored state and 76 % in the bleached state.

1. Introduction

The domain of electrochromic devices (ECDs) is an exciting and fast growing field of research [1-5]. While some ECDs already reached commercialization long ago (*e.g.*, rear- and side-view mirrors and sunroofs for automobile glazing, sunglasses and aircraft canopies with controllable optical transmission), current developments in the domain of ECDs are entirely governed by energy saving requirements and the interests have shifted rapidly from non-architectural applications toward the production of large area devices for application in smart switchable and energy efficient architectural glazing, privacy glass, partitions and skylight.

A conventional solid state ECD comprises three main elements arranged in a layered, "sandwish"-type configuration composed of an electrochromic electrode and a counter-electrode separated by a solid electrolyte (*e.g.*, a Li^+ , K^+ or H^+ conducting polymer). A persistent and reversible color switch occurs by charging/discharging the electrochemical cell through the application of an electrical potential. The colored and transparent states of ECDs are usually designated as "written" and "bleached" states, respectively. The most widely used electrochromic (EC) material is tungsten trioxide (WO_3) which undergoes a reversible color change as a result of simultaneous injection

and extraction of electrons and ions (double injection) [6]. EC materials may operate either in a reflective mode (displays) or transmissive mode ("smart windows"). An attractive feature of ECDs is that once they are colored, the current may be turned off and the color preserved (*memory effect*), making them energy efficient devices.

In the last few years the versatile sol-gel process [7] has become a popular synthetic route for ECD fabrication. In particular it has opened new opportunities for obtaining advanced, functional and high EC quality coatings with adequate optical, chemical, electrooptical and mechanical properties [8-15]. The sol-gel method offers many advantages with respect to traditional techniques in the context of coating technology: (1) A high degree of homogeneity of the films is achieved, since the starting precursors are mixed at the molecular level. (2) The precursors are relatively cheap and a large variety is commercially available. (3) The deposition equipment is inexpensive and large coatings can be obtained by several techniques, such as spin-coating, dip-coating and spraying.

The first application of the "all sol-gel" ECD concept is thought to have taken place in 1988 with the pioneering work of Judeinstein et al. [16]. The device, with configuration WO_3│titanium oxide (TiO_2) gel│tin oxide (SnO_2), failed due to irreversible SnO_2 coloration. The first successful "all sol-gel" ECD was reported in 1994 by Macêdo and Aegerter [17] who used a WO_3│TiO_2 gel│cerium oxide $(CeO_2)/TiO_2$ configuration.

Several organic-inorganic hybrid electrolyte materials [18] have been obtained *via* the sol-gel route. The use of *ormolytes* - the acronym of organically modified silicate electrolytes - in ECDs is quite attractive because these materials are essentially amorphous and highly transparent, they exhibit good mechanical properties and improved chemical/thermal stability. In addition, Class II**Erro! Marcador não**

definido. [18] ormolytes can accommodate greater quantities of guest salt than polymer electrolytes (PEs) [19], thus avoiding the prejudicial effects of "salting out" on device performance.

A reduced number of proton conducting Class I hybrid systems have been proposed as electrolytes for ECDs. Examples are the hybrid gels made from tetrabutoxytitane(IV), acetic acid and glycerol [16] and the amorphous tallium oxide multi-layers dip-coated from tetraethoxytallane(IV), using acetic acid or H_2O as a stabilizer [20]. The proton conducting Class II *aminosil* ormolytes [21-22] [23] were also considered to be good candidates for "smart windows". These materials comprise a basic hybrid structure formed from aminopropylalkoxysilanes and a strong monoacid. The highest conductivity reached was *ca.* $3x10^{-5}$ Scm^{-1} at room temperature. An electrochemical stability domain of 1.3 V was reported for the aminosils doped with trifluoromethanesulfonic acid. A quite significant amount of Li^+ conducting Class II ormolyte systems have been investigated in the same context [24-25] [26-28]. The high ionic conductivity exhibited by classical poly(oxyethyelene) (POE)-based PEs incorporating K^+ ions [29-31] [32] motivated the investigation of ormolytes composed of di-urea cross-linked poly(oxypropylene)/siloxane [33] and POE/siloxane [34-35](*di-ureasil*) matrices and potassium salts. The di-ureasils composed of long POE chains and doped with potassium triflate (KCF_3SO_3) were proposed as electrolytes for the fabrication of "smart windows" [35].

In view of their use as electrolytes in ECDs, we have synthesized and characterized in the present work we have prepared and characterized a novel series of environmentally friendly KCF_3SO_3-doped biohybrids composed of a di-urethane cross-linked siloxane-based host network incorporating short segments of the poly(ε-caprolactone) biopolymer, abbreviated as PCL(530) (530 represents the average molecular weight in g

mol^{-1}). This investigation is a continuation of a study initiated earlier devoted to the PCL(530)/siloxane family doped with lithium triflate (LiCF$_3$SO$_3$) [36], magnesium triflate (Mg(CF$_3$SO$_3$)$_2$) [37] and a 50:50 molar mixture of LiCF$_3$SO$_3$ and europium triflate (Eu(CF$_3$SO$_3$)$_3$) [38].

PCL, a linear poly(ester), has been chosen because, although synthetic, it is an extremely attractive biopolymer. It is an aliphatic thermoplastic, biocompatible, permeable, hydrophobic, biodegradable and non-toxic for living organisms, which is resorbed after a certain period of implantation time. PCL and its copolymers have potential application in the field of medicine, as biodegradable suture, artificial skin, resorbable prostheses and containers for sustained drug delivery [39-41]. PCL/silica hybrids may find use as degradable bioglasses, coating materials for bone implants and prosthetic devices, as supports for enzyme immobilization [42] and as bone substitutes [43].

In recent years there has been a growing interest in biopolymers, as they represent viable alternatives for the development of the so-called electroactive polymers (EAPs) [44]. Most bio-based EAPs are ion conducting materials. It is the case of the systems comprising hydroxyethylcellulose, [45] modified starch, [46] chitosan [47] [48] [49-51] [52] or natural rubber [53] and ionic salts. Small all solid-state ECDs with good electrochromic properties have been successfully produced with EAPs composed of cellulose [54], starch [55, 56] and gelatin [57].

2. Experimental

2.1. Materials

α,ω− hydroxyl poly(ε-caprolactone) (PCL(530), Fluka, average molecular weight 530 g/mol) and 3-isocyanatepropyltriethoxysilane (ICPTES, Fluka) and KCF_3SO_3 (Aldrich) were used as received. Ethanol (CH_3CH_2OH, Merck) and tetrahydrofuran (THF; Merck) were stored over molecular sieves. High purity distilled water was used in all experiments.

To prepare the KCF_3SO_3-doped d-PCL(530)/siloxane-based biohybrids we adopted the synthetic method described elsewhere [58], which is a modification of that reported for the $LiCF_3SO_3$-doped analog [36]. The ormolytes, identified using the notation d-PCL(530)/siloxane$_n$KCF$_3$SO$_3$, were obtained as transparent, flexible monoliths with a slightly yellowish hue. Xerogels with n = ∞, 200, 100, 40 29, 21, 10, 4, 2, 1 and 0.5 were prepared. Experimental details of the synthetic procedure are collected in Table 1.

2.2. Characterization

XRD measurements were performed at room temperature with a PANalytical X'Pert Pro equipped with a X'Celerator detector using monochromated CuK_α radiation (λ = 1.541 Å) over the 2θ range between 10 and 70 °. The samples, analyzed as films, were not submitted to any thermal pre-treatment.

To evaluate the morphology of the as-prepared xerogel samples, SEM micrographs were obtained using a SEM/ESEM-FEI Quanta 400 scanning electron microscope at high acceleration voltage (25 kV).

Samples for thermogravimetric studies were transferred to open platinum pans and analysed using a TA Instruments Q50 thermobalance at a heating rate of 10 ºC min^{-1} from room temperature up to 700 ºC. Prior to measurement, the samples were vacuum-

dried over phosphorus pentoxide (P_2O_5) for several days. The thermal characteristics of the xerogels were also determined using a Setaram DSC 131 Differential Scanning Calorimeter. A disk section with a mass of approximately 20-30 mg was removed from the biohybrid film, placed in 40 µl aluminium can and stored in a dessicator over P_2O_5 for one week at room temperature under vacuum. After this drying treatment the can was hermetically sealed and the thermograms was recorded. Each sample was heated from 25 to 250 ºC at 10 ºC min^{-1}. High purity nitrogen at a constant flow rate of 40 cm^3 min^{-1} (TGA) and 35 cm^3 min^{-1} (DSC) was used as purging gas in both experiments.

Prior to characterization of conductivity behavior, the ormolytes were vacuum-dried at 80ºC for about 48 h and stored in a high-integrity, argon-filled glove box. For bulk conductivity measurements, an ormolyte disk was placed between two 10 mm diameter ion-blocking gold electrodes (Goodfellow, > 99.9%). The electrode/ormolyte/electrode assembly was secured in a suitable constant-volume support, which was installed in a Buchi TO 51 tube oven. A calibrated type K thermocouple, placed close to the ormolyte disk, was used to measure the sample temperature with a precision of about ± 0.2 ºC and samples were characterized over a temperature range of between 25 and 100 ºC. Bulk conductivities of the samples were obtained during heating cycles using the complex plane impedance technique (Schlumberger Solartron 1250 frequency response analyser and 1286 electrochemical interface) over a frequency range of 65 kHz to 0.5 Hz. The electrolyte behavior was found to be almost ideal and bulk conductivities were extracted in the conventional manner from impedance data by using an equivalent circuit composed of R_b in parallel with C_g, where R_b is the electrical resistance of the electrolyte and C_g is its geometric capacity. The circuit element corresponding to the blocking electrode interface was simulated by a series C_{dl} element, where C_{dl} in the double layer capacity. The experimental spectra showed a high frequency semicircle

with a low frequency vertical spike. Reproducibility of measurements was better than 5%.

The Fourier-Transform infrared (FT-IR) spectra were acquired at room temperature using a Unicam FT-IR spectrophotometer. The spectra were collected over the 4000-500 cm^{-1} range by averaging 64 scans at a wavenumber resolution of 4 cm^{-1}. Solid samples (2 mg) were finely ground, mixed with approximately 175 mg of dried potassium bromide (KBr, Merck, spectroscopic grade) and pressed into pellets.

The FT-Raman spectra were recorded at room temperature with a Bruker RFS 100/S spectrometer equipped with a near-infrared Nd:YAG laser with wavelength excitation (1064 nm at 400 mW). The spectra were collected over the 3200–300 cm^{-1} range by averaging 200 scans at a maximum resolution of 4 cm^{-1}.

To deconvolute complex band envelopes, the non-linear curve-fitting procedure offered by the PeakFit software (Jandel Corporation, 2591 Rerner Boulevard, San Rafael, CA 94901, U.S.A.) was employed. To automatically place hidden peaks, the residuals procedure was used. This procedure initially places peaks by finding local maxima in a smoothed data stream. Hidden peaks are then optionally added where peaks in the residuals occur. The best fit of the experimental data was obtained by varying the parameters of the bands (*i.e.*, wavenumber, width and intensity) and by using Gaussian functions. A linear baseline correction with a tolerance of 3 % was employed. The standard error of the curve-fitting procedure was less than 0.003.

Solid-state ECDs were constructed using a four layer sandwich configuration which did not include an ion storage layer (Scheme 1). The external layers of the ECDs were transparent conducting oxide films made of indium-doped zinc oxide (IZO) [59]. The active layers of the ECDs were an EC film of tungsten oxide (WO_3) and an d-PCL(530)/siloxane$_n$KCF$_3$SO$_3$ ormolyte film with n = 29, 21 and 4. IZO films with a

thickness 170 nm were deposited on two glass substrates by r. f. (13.56 MHz) magnetron sputtering using a ceramic oxide target In_2O_3:ZnO (92:8 wt%; 5 cm-diameter, Super Conductor Materials, Suffern, NY, U.S.A., purity of 99.99%). Sputtering was carried out at room temperature, with an argon flow of 20 cm^3 min^{-1} and an oxygen flow of 0.4 cm^3 min^{-1}. During sputtering the deposition pressure (argon and oxygen) was held constant at 0.15 Pa. The distance between the substrate and the target was 10 cm and the r. f. power was maintained at 100 W. WO_3 (Super Conductor Materials, purity of 99.99%) films with thickness of about 300 nm were deposited on the IZO-coated glass substrates by r. f. magnetron sputtering (Pfeiffer Classic 500). Two drops of the ormolyte sol were then spread onto the surface of the WO_3/IZO-coated glass plates and a IZO-coated glass plate was placed on top of the resulting ormolyte gel and the two plates were pressed together in such a way that the two coatings faced each other inside the assembled system (Scheme 1). In this manner a surface with an area of approximately 2.7 cm^2 was formed. Free space was left on each side for the electrical contacts. The entire assembly procedure described was carried out under atmospheric conditions. Under the application of a negative voltage of -4 V during 30 s to each glass/IZO/WO_3/d-PCL(530)/siloxane$_n$KCF$_3$SO$_3$/IZO/glass ECD the color of WO_3 changed from light yellow to uniform dark blue (Scheme 1). During coloration charge in the form of electrons and K^+ ions was transferred from the IZO and ormolyte films, respectively, to WO_3 which suffered simultaneously reduction and K^+ insertion. Bleaching from deep blue back to light yellow (Scheme 1), corresponding to simultaneous WO_3 oxidation and K^+ desinsertion, occurred upon reversing the applied voltage.

The optical transmittance of the ECDs was measured with a Shimadzu UV/VIS 3100PC double beam spectrophotometer and with UV-VIS Spectronic Genexys 2PCC spectrophotometer.

3. Results and discussion

3.1. Structure and morphology

The XRD patterns of the d-PCL(530)/siloxane$_n$KCF$_3$SO$_3$ biohybrids are reproduced in Figure 1. The diffractograms of the samples with n = ∞, 100 and 40 reveal that these xerogels are entirely amorphous. The broad peak, Gaussian in shape, centered at *ca.* 21.3-21.6°, observed in these patterns is ascribed to ordering within the siliceous network [60]. The dilute sample with n = 200 gives rise to a peak at 21.4 °, which is characteristic of PCL(530). The same feature appears as an ill-defined peak in the XRD patterns of the materials with n = 21 and 10. For n = 29 and 21 a Bragg reflection of unknown nature emerges at 28.5 °. The concentrated sample with n = 4 produces a series of weak peaks which do not correspond to those of the pure salt or PCL(530). We associate them with the formation of a crystalline d-PCL(530)/siloxane-KCF$_3$SO$_3$ complex of unknown stoichiometry. In the salt-rich samples with n = 2, 1 and 0.5 this crystalline compound coexists with pure salt.

The SEM images obtained, shown in Figure 2, are in perfect agreement with the XRD data. The occurrence of crystalline PCL(530) regions is confirmed in Figures 2(a)-2(c). Small crystalline aggregates, presumably due to the formation of the crystalline d-PCL(530)/siloxane-KCF$_3$SO$_3$ complex, are observed at n = 4 (Figure 2(d)). The high crystalline content of the two most concentrated xerogels is immediately recognized in Figures 2(e) and 2(f).

3.2. Thermal analysis

The DSC curves of the d-PCL(530)/siloxane$_n$KCF$_3$SO$_3$ xerogels with n $\leq$ 10 are represented in Figure 3. In the case of the samples with n = 10 and 2 a very weak, broad and ill-defined endothermic peak at 45 ºC (onset at 42 ºC) is distinctly detected. This thermal event is due to the fusion of the short polymer segments of PCL(530) (melting temperature 36-48 ºC), thus corroborating the XRD data. The salt-rich biohybrid with n = 1 produces a weak, broad and ill-defined endotherm at 146 ºC (onset at 132 ºC), of unknown origin, and a stronger one at 225 ºC (onset at about 200 ºC). The latter peak becomes more intense at n = 0.5. On the basis of the conclusions retrieved from the XRD results, we propose that this endothermic event receives a major contribution from the melting peak of the d-PCL(530)/siloxane-KCF$_3$SO$_3$ complex and a minor contribution from the melting peak of the pure salt which is located at 237 ºC (onset at 228 ºC) (Figure 3).

The TGA data of Figure 4 allow us to infer that the decomposition of the xerogels with ∞ > n $\geq$ 1 is initiated at about the same temperature (approximately 235 ºC), an indication that the thermal stability of the PCL(530)/siloxane framework in a non-oxidizing atmosphere remains practically unaffected by the presence of increasing amounts of KCF$_3$SO$_3$. The thermal degradation of the most concentrated material (n = 0.5) begins, however, at a considerably lower temperature (*ca.* 200 ºC). The thermal behavior of the hybrid samples was very different from that of KCF$_3$SO$_3$ which starts to undergo degradation only beyond 450 ºC. It is worth noting that at the maximum temperature analyzed here, *i.e.*, 700 ºC, none of the samples were completely decomposed.

3.3. Ionic conductivity and ionic interactions

The Arrhenius conductivity plot and the composition dependence of the conductivity isotherms of the d-PCL(530)/siloxane$_n$KCF$_3$SO$_3$ samples are shown in Figures 5(a) and 5(b), respectively. These data reveal that in this hybrid system the samples with n = 21 and 4 lead to the highest conductivities over the whole range of temperatures analyzed. At 40 ºC the conductivity maximum coincides, whereas at higher temperature the material with n = 21 leads to slightly higher values. Table 2 demonstrates that the levels of ionic conductivity exhibited by the K$^+$-doped d-PCL(530)/siloxane-based hybrids are lower than those displayed by the analogue biohybrids incorporating LiCF$_3$SO$_3$ [36] and a 50:50 molar mixture of LiCF$_3$SO$_3$ and Eu(CF$_3$SO$_3$)$_3$ [38], but higher than those measured in the case of the MgCF$_3$SO$_3$-containing materials [37].

In an attempt to clarify the ionic conductivity/ionic association relationship, we decided to inspect the chemical surrounding experienced by the K$^+$ and SO$_3$CF$_3^-$ ions in the d-PCL(530)/siloxane medium over the entire salt concentration range considered. We emphasize that in this sort of hybrid system the guest alkaline ions may bond, not only to the triflate ions, but also to the three types of donor oxygen atoms provided by the d-PCL(530)/siloxane network, *i.e.*, the carbonyl oxygen atoms of the urethane cross-links, the ester carbonyl oxygen atoms of the PCL(530) chains and the ether oxygen atom of the PCL(530) central oxyethylene moiety.

The coordination of the cation to the urethane and ester carbonyl groups of the host matrix is manifested in the "amide I" region which corresponds to the amide I [61] region of polyamides [62]. The amide I mode is essentially a carbonyl stretching vibration [62]. Because of its sensitivity to hydrogen bonding, the amide I band is in

general composed of several distinct components which correspond to different carbonyl environments (aggregates). As the absorption coefficients of the carbonyl groups from these aggregates may differ, only changes of the same component as a function of salt concentration may be compared [63].

Curve-fitting, performed in the 1800-1650 cm^{-1} interval of the FT-IR spectra of the d-PCL(530)/siloxane$_n$KCF$_3$SO$_3$ xerogels, allowed us to resolve the band profile of the d-PCL(530)/siloxane hybrid into four distinct components located at about 1762, 1736, 1720 and 1692 cm^{-1} (Figure 6(a)).[58] [64]. The 1762 cm^{-1} band is associated with the presence of "free" (non-hydrogen bonded) carbonyl groups of the urethane cross-links [65]. The 1736 cm^{-1} component is characteristic of amorphous PCL(530) chains [66-67]. The band at 1720 cm^{-1} is attributed to the presence of hydrogen-bonded oxyethylene/urethane associations [68], whereas that at 1692 cm^{-1} is assigned to the formation of urethane/urethane [68] and ester/urethane [[58, 64] aggregates. The four types of carbonyl groups have been represented by the notations **A1**, **A2**, **B**, **C1** and **C2**, respectively [65].

The general "amide I" band profile of the non-doped and doped d-PCL(530)/siloxane hybrid materials with n ≤ 29 (Figures 6(a) and 6(b)) is essentially the same (the intensity maximum is located in all cases around 1736 cm^{-1}). The further addition of salt alters the band shape and the intensity maximum is shifted to 1731 cm^{-1} for n = 10 and 4 and to 1725 cm^{-1} for n = 21, 1 and 0.5 (Figures 6(a) and 6(b)), suggesting that the hydrogen bonds are globally stronger in the latter three samples. We draw the attention to the fact that carbonyl groups **A1** exist in all the materials.

Curiously, the plot of Figure 6(c) demonstrates that the proportion of "free" carbonyl groups **A1** and **A2** practically coincides in the non-doped network and in the most concentrated sample. The trends observed in this graph also suggest that the

destruction/formation of aggregates **B**, which results from the addition of increasing amounts of salt, is correlated with the formation/destruction of aggregates **C1** and/or **C2**. Although the introduction of the alkaline metal salt affects the "amide I" region over the entire range of compositions, the most significant modifications undergone by the "amide I" components take place in d-PCL(530)/siloxane$_{29}$KCF$_3$SO$_3$. This hybrid contains the lowest proportion of carbonyl groups **A1** and the highest fraction of carbonyl groups **A2** of all the series, an indication that the strong hydrogen-bonded aggregates formed at this composition are probably aggregates **C1**. In the high salt concentration range (n = 1 and 0.5), the formation of aggregates **B** is clearly favoured. At this composition, the fraction of aggregates **C1** and **C2** is fairly low.

The examination of the anionic environment was carried out by means of FT-Raman spectroscopy. We examined the spectral region characteristic of the symmetric stretching vibration mode of the SO$_3$ group (ν_sSO$_3$), since this diagnostic mode is very sensitive to coordination effects. The ν_sSO$_3$ mode of the "free" triflate ion gives rise to a band at 1032 cm^{-1} [69]. Typically the coordination of the triflate ion to the K$^+$ ion is manifested as a shift to higher wavenumbers [32].

The FT-Raman ν_sSO$_3$ region was decomposed into several peaks (Figure 7(a)). The most prominent band for the most diluted samples (n ≤ 10) is that at 1032 cm^{-1}. This feature, which is present over the whole salt concentration range, confirms the occurrence of "free" anions and presumably "cross-link separated ion pairs" [65, 68]. The contribution of the latter species might explain the remarkable increase of the band integral area fraction at 40 > n ≥ 10 (Figure 7(b)). The 1038 and 1024 cm^{-1} features, also produced by all the samples, are associated with weakly coordinated triflate ions located in two different sites [68]: (1) CF$_3$SO$_3^-$ species weakly bonded to K$^+$ ions, which simultaneously interact with the carbonyl oxygen atom of the urethane group; (2)

$CF_3SO_3^-$ ions hydrogen bonded to the urethane N-H groups. The event at 1045 cm^{-1}, found in all the FT-Raman spectra, is ascribed to the existence of contact ion-pairs [[35]]. The components produced by the hybrid with n = 40 at 1069, 1059 and 1052 cm^{-1} are tentatively attributed to the formation of higher ionic aggregates [70] [35]]. Interestingly, at n = 10 none of these coordinated species are formed. In the v_sSO_3 region of the two most concentrated samples, the 1052 cm^{-1} band is the most intense feature. Based on the XRD and DSC results, we suggest that in both cases free crystalline KCF_3SO_3 contributes to this feature [[35]].

The examination of the plot of Figure 7(b) does not allow us to establish a direct correlation between the high room temperature ionic conductivity exhibited by the d-PCL(530)/siloxane$_{21}$KCF$_3$SO$_3$ sample and the proportion of "free" anions and/or weakly-coordinated species. In fact, samples with n = 29 and 10 contain similar amounts of such species and exhibit, however, considerably lower conductivity. The ionic conductivity is the result of a balance between two contributions: the concentration of charge carriers and their mobility. Clearly, in the materials investigated ionic association is considerable.

3.4. Electrocromic device characterization

The glass/IZO/WO$_3$/d-PCL(530)/siloxane$_n$KCF$_3$SO$_3$/IZO/glass ECDs with n = 29, 21 and 4 were characterized in terms of the electrochromic contrast (percent transmittance change (Δ T) in % at a particular wavelength or wavelength range), the optical density change ($\Delta(OD) = -\log(T_{colored}/T_{bleached})$), the switching time (the time neede for the coloring/bleaching process) and the open circuit memory (the ability to hold the absorption state while the current is off).

The transmission spectra recorded in the 325-700 nm range for the glass/IZO/WO$_3$/d-PCL(530)/siloxane$_n$KCF$_3$SO$_3$/IZO/glass ECDs with n = 29, 21 and 4 in the as-deposited, bleached and colored states are depicted in Figures 8(a), 8(b) and 8(c), respectively. The 1931 CIE photopic luminosity function, with a maximum at a wavelength of 555 nm (green), is also reproduced in Figure 8 (see dotted curve). All the spectra represented in Figure 9 display a series of maxima and minima due to interference associated with the ECDs multilayer configuration (Scheme 1). The average Δ T in the visible (VIS) region (400-700 nm) and the optical density change Δ(OD) exhibited by the three ECDs are listed in Table 2. We note that the average Δ T of the as-deposited and bleached states are practically the same in the three cases, the value being higher than 74 % for the bleached devices (Figure 8 and Table 3). After coloration the three samples present a Δ(OD) above 0.11.

The switching speed of the ECDs studied in the present work is fast (t $\approx$ 30 s, see Experimental section).

The electrochromic memory of the glass/IZO/WO$_3$/d-PCL(530)/siloxane$_n$KCF$_3$SO$_3$/IZO/glass ECDs with n = 4 and 29 was evaluated. Figures 9(a) and 9(b) show that after 10 days both devices did not reach the as-deposited non-colored state.

4. Conclusions

A series of di-urethane cross-linked PCL(530)/siloxane biohybrids doped with KCF$_3$SO$_3$ have been characterized by XRD, SEM, DSC, TGA, ionic conductivity, FT-IR and FT-Raman spectroscopy. Preliminary studies of the performance of prototype

Solid State Ionics

ECDs including these xerogel materials as electrolytes demonstrated that further investigation on these materials is fully justified.

Acknowledgements

References

1. C. M. Lampert, A.A., C. Baertien, J. Nagai, *Durability evaluation of electrochromic devices - an industry perspective.* Solar Energy Materials & Solar Cells 1999. **56**: p. 449-463.
2. B. Orel, A.Š., U. Opara Krašovec, *Recent progress in sol-gel derived electrochromic devices.* Acta Chim. Slov. , 1998. **45**(4): p. 487-506.
3. J. Livage, D.G., *Sol}gel electrochromic coatings and devices: A review.* Sol. Energy Mater. Sol. Cells, 2001. **68**: p. 365-381.
4. Mortimer, R.J., *Electrochromic materials.* Chem. Soc. Rev., 1997. **26**: p. 147-156.
5. O. Lev, Z.W., S. Bharathi, V. Glezer, A. Modestov, J. Gun, L. Rabinovich, S. Sampath, *Sol-Gel Materials in Electrochemistry.* Chem. Mater, 1997. **9**: p. 2354-2375.
6. C. G. Granqvist, *Handbook of Inorganic Electrochromic Materials.* 2nd ed. 2002, Amsterdam: Ed. Elsevier.
7. C. J. Brinker, G.W.S. and *Sol-gel Science: The Physics and Chemistry of Sol-Gel Processing.* 1990, San Diego: Academic Press.
8. D. Keomany, C.P., D. Deroo, Sol. Energy Mater. Sol. Cells, 1994. **33**: p. 429.
9. M. A. Aegerter, R.A., A. Soutar, K. Tadanaga, H. Yang and T. Watanabe, *Coatings made by sol–gel and chemical nanotechnology.* J. Sol-Gel Sci. Tech., 2008. **47**: p. 203-236.
10. B. Munro, S.K., P. Zapp, H. Krug, J. Sol-Gel Sci. Tech., 1998. **13**: p. 673-678.
11. C. O. Avellaneda, A.P., M. Schmitt, S. Heusing, M. A. Aegerter, Ceram. Trans., 1998. **81**.

12. M. Schmidt, S.H., M. A. Aegerter, A. Pawlicka, C. O .Avellaneda, Sol. Energy Mater. Sol. Cells, 1998. **54**.

13. Bange, K., *Colouration of tungsten oxide "lms: A model for optically active coatings.* Solar Energy Materials & Solar Cells 58 (1999) 1}131, 1999. **58**: p. 1-131.

14. L. O. Melo, C.O.A., A. Pawlicka, *Sol-Gel Coatings of Nb 2O5 and Nb2 0 5: Li+ Electrochemical and Structural Characterization.* Mol. Cryst. Liq. Cryst., 2002. **374**: p. 101-106.

15. A. Patra, K.A., D. Ganguli, J. Livage, P. K. Biswa, *Sol–gel electrochromic WO 3 coatings on glass.* Mater. Lett., 2004. **58**: p. 1059-1063.

16. P. Judeinstein, J.L., A. Zarudiansky, R. Rose, Solid State Ionics, 1998. **28-30**: p. 1722.

17. M. A. Macêdo, M.A., *Sol-Gel Electrochromic Device.* J. Sol-Gel Sci. Tech., 1994. **2**: p. 667-671.

18. Sanchez, P.G.-R.a.C., *Functional Hybrid Materials*, ed. P.G.-R.a.C. Sanchez. 2003, New York: Wiley Interscience.

19. F. M. Gray, P.E. 1997, London: The Royal Society of Chemistry.

20. A. Kishimoto, T.K., T. Namba, *Amorphous tantalum and niobium oxide proton conductors derived from respective peroxo polyacids* Solid State Ionics, 1992. **53-56**: p. 993-997.

21. Rousseau, F. 1990, University of Grenoble: Grenoble.

22. F. Rousseau, C.P., J. Garcia, M. Popall, *Polycondensation of Aminosilanes in Methanol.* Chem. Mater., 1995. **7**: p. 828-839.

23. H. Schmidt, M.P., F. Rousseau, C. Poinsignon, M. Armand and J.-Y. Sanchez in *Second International Symposium on Polymer Electrolytes*. 1989. Siena, Italy: Elsevier Applied Science.

24. P. C. Barbosa, M.M.S., M. J. Smith, A. Gonçalves, E. Fortunato, *Studies of solid-state electrochromic devices based on PEO/siliceous hybrids doped with lithium perchlorate.* Electrochimica Acta, 2007. **52**: p. 2938-2943.

25. P. C. Barbosa, M.M.S., M. J. Smith, A. Gonçalves, E. Fortunato, S. C. Nunes, V. De Zea Bermudez, *Di-ureasil xerogels containinh lithium bis(trifluoromethanesulfonyl)imide for application in solid state electrochromic devices.* Electrochim. Acta, 2009. **54**: p. 1002-1009.

26. Paula C. Barbosa, M.F., Sérgio M. F. Vilela, A. Gonçalves, M. C. Oliveira, E. Fortunato, M. Manuela Silva, Michael J. Smith, R. Rego, Verónica de Zea Bermudez, *Di-Ureasil Hybrids Doped with LiBF4: Attractive Candidates as Electrolytes for "Smart Windows".* Int. J. Electrochem. Sci., 2011.

27. L.C. Rodrigues, P.C.B., M.M. Silva, M.J. Smitha, A. Gonçalves, E. Fortunato, *Application of hybrid materials in solid-state electrochromic devices* Optical Materials, 2009. **31**(10): p. 1467-1471.

28. M.M. Silva , P.C.B., L.C. Rodrigues, A. Gonçalves, C. Costa, E. Fortunato, *Gelatin in electrochromic devices* 2010. **32**(6): p. 719-722.

29. Chabagno, J.M. 1980, University of Grenoble.

30. S. Besner, A.V., G. Bouchard, J. Prudhomme, *Effect of Anion Polarization on Conductivity Behavior of Poly(ethy1ene oxide) Complexed with Alkali Salts.* Macromolecules, 1992. **25**: p. 6480-6488.

31. J.-G. Béraud. 1993, University of Grenoble

32. S. Chintapalli, C.Q., R. Frech, C. A. Vincent, *Compound Formation and Ionic Association in the Poly(ethylene oxide)−Potassium Triflate System.* Macromolecules, 1997. **30**: p. 7472-7477.

33.   J. Chaker, K.D., V. C Briois, V. Santilli, S. H. Pulcinelli, P. Judeinstein, J. Sol-Gel Sci. Tech., 2003. **26**: p. 1075-1080.

34.   V. de Zea Bermudez, S.M.G.C., M. M Silva, S. Barros, M. J. Smith, R. A. Sá Ferreira, L. D. Carlos, C. Molina, S. J. L. Ribeiro, J. Sol-Gel Sci. Tech., 2003. **26**: p. 1-7.

35.   S. C. Nunes, V.d.Z.B., M. M Silva, M. J. Smith, D. Ostrovskii, R. A. Sá Ferreira, L. D. Carlos, J. Rocha, A. Gonçalves, E. Fortunato, *Sol-gel derived potassium based di-ureasils for "smart windows".* J. Mater. Chem., 2007. **17**: p. 4239-4248.

36.   S. C. Nunes, V.d.Z.B., M. M. Silva, M. J. Smith, E. Morales, L. D. Carlos, R. A. Sá Ferreira, J. Rocha *Sol-gel derived Li -doped biohybrid electrolytes.* J. Solid State Electrochem, 2006. **10**: p. 203-210.

37.   J.C.S. Teixeira, M.F., V. de Zea Bermudez , P.C. Barbosa, L.C. Rodrigues, M.M. Silva, M.J. Smith, *Mg2+-doped poly(.-caprolactone)/siloxane biohybrids.* 2010. **55**: p. 1328-1332.

38.   M. Fernandes, S.S.N., L. C. Rodrigues, A. Gonçalves, R. Rego, M. C. Oliveira, R. A. S. Ferreira, E. Fortunato, M. M. Silva, L. D. Carlos, V. de Zea Bermudez, *Li+- and Eu3+-doped poly(ℳ-caprolactone)/siloxane biohybrid electrolytes for electrochromic devices.* 2011.

39.   J. Pak, J.L.F., C. Rostron, V. Walters, Pharm. Acta Helv., 1985. **160**: p. 160.

40.   D. W. Grijpma, G.J.Z., A. J. Penning, *High molecular weight copolymers of l-lactide and ε-caprolactone as biodegradable elastomeric implant materials* Polymer Bulletin, 1991. **25**: p. 327-333.

41.   A. G. A. Coombes, S.C.R., M. Williamson, J.E. Barralet, S. Downes, W.A. Wallace, *Precipitation casting of polycaprolactone for applications in tissue engineering and drug delivery* Biomaterials, 2004. **25**: p. 315-325.

42.   D. Tian, P.D., R. Jérôme, , 37(17) (1996) *A new poly(ε-caprolactone) containing hybrid ceramer prepared by the sol-gel process.* Polymer, 1996. **37 (17)**: p. 3983-3987.

43.   S.-H. Rhee, J.-J.C., H.M. Ki, *Preparation of a bioactive and degradable poly(epsilon -caprolactone)/silica hybrid through a sol-gel method.* Biomaterials, 2002. **23**: p. 4915-4921.

44.   Finkenstadt, V., App. Microbiol. Biotecnol., 2005. **67**: p. 735.

45.   C.E. Tambelli, J.P.D., A.M. Regiani, A. Pawlicka, A. Gandini, J. F. LeNest, *Nuclear magnetic resonance and conductivity study of HEC:polyether-based polymer electrolytes.* Electrochim. Acta, 2001. **46** p. 1665-1672.

46.   A. Pawlicka, D.C.D., C. O. Avellaneda *Molecular Low Dimensional and Nanostructured Materials for Advanced Applications.* Kluver Academic Publishers in the NATO ASI Series, ed. R.B. A. Graja, F. Kajzar. 2002. 255.

47.   N. S. Mohamed, R.H.Y.S., A. K. Arof *Polymer batteries fabricated from lithium complexed acetylated chitosan* J. Power Sources, 1995. **56**: p. 153-156.

48.   N. M. Morni, N.S.M., A. K. Arof, Mater. Sci. Eng., 1997. **B45**: p. 149.

49.   N. M. Morni, N.S.M., A. K. Arof, Mater. Sci. Eng. B45 (1997) 140; (c) Z. Osman, Z. A. Ibrahim, A. K. Arof, , Carbohydr. Polym., 2001. **44**: p. 167.

50.   Z. Osman, A.K.A., *FTIR studies of chitosan acetate based polymer electrolytes.* Electrochimica Acta, 2003. **48** p. 993-999.

51.   S. R. Majid, A.K.A., Physica B, 2005. **355** p. 78.

52.   N. H. Idris, S.R.M., A. S. A. Khiar, M. F. Hassan, A. K. Arof, *Conductivity Studies on Chitosan/PEO Blends with LiTFSI Salt.* Ionics, 2005. **11**: p. 375-377.

53.   M. D. Glasse, R.I., R. J. Latham, R. G. Linford, W. S. Schlindwein, Solid State Ionics, 2002. **147**: p. 289-294.

54.   A. Pawlicka, D.C.D., K. V. Guimaraes, C. O. Avellaneda, *Electochromic devices with solid electrolytes based on natural polymers.* Mol. Cryst. Liq. Cryst., 2004. **416**: p. 105/[361]-112/[368].

55.   R. G. F. Costa, C.O.A., A. Pawlicka, S. Heusing, M.. A. Aegerter, Mol. Cryst. Liq. Cryst., 2006. **447**: p. 45.

56.   A. S. Ahmad Khiar, A.K.A., *Conductivity studies of starch based polymer electrolytes*
2009.

57.   S. C. de Oliveira, L.d.M., A. A. S. Curvelo, R. M. Torresi, J. Electrochem. Soc., 2003. **150**: p. E578.

58.   M. Fernandes, V.d.Z.B., R. A. Sá Ferreira, L. D. Carlos, A. Charas, J. Morgado, M. M. Silva, M. J. Smith, Chem. Mater., 2007. **19**(16).

59.   E. Fortunato, L.P., P. Barquinha, I. Ferreira, R. Prabakaran, G. Goncalves, A. Goncalves, R. Martins, Philos. Mag., 2009. **89**: p. 2741.

60.   L. D. Carlos, V.d.Z.B., R, A. Sá Ferreira, L. Marques, M. Assunção, *Sol-Gel Derived Urea Cross-Linked Organically Modified Silicates. 2. Blue-Light Emission.* Chemistry of Materials, 1999. **11**: p. 581-588.

61.   T. Miyazawa, T.S., S.-I. Mizushima, J. Chem. Phys., 1956. **24**(2): p. 408-418.

62.   D. J. Skrovanek, S.E.H., P. C. Painter, M. M. Coleman Macromolecules, 1985. **18**: p. 1676-1683.

63.   M. M. Coleman, K.H.L., D. J. Skrovanek, P. C. Painter, Macromolecules, 1986. **19**: p. 2149-2157.

64.   S. C. Nunes, V.d.Z.B., D. Ostrovskii, N. V. Martins, *Vibrational Spectra and microstructure of poly(e-caprolacyone)/siloxane biohybrids doped with lithium triflate.* Journal of Molecular Structure, 2008. **879**: p. 73-80.

65.   Verónica de Zea Bermudez, D.O., Sergei Lavoryk,M. Cristina Gonçalves, Luís D. Carlos, *Urethane cross-linked poly(oxyethylene)/siliceous nanohybrids doped with Eu3+ ions Part 2.Ionic association.* Phys. Chem. Chem. Phys., 2004. **6**: p. 649-658.

66.   Y. He, Y.I., Polym. Int., 2000. **49**: p. 623.

67.   A. Sanchis, M.G.P., C. Salom, R. M. Masegosa, J. Polym. Sci. Polym. Phys. Ed,, 1979. **17**: p. 837.

68.   Verónica de Zea Bermudez, D.O., M. Cristina Gonçalves, Luis D. Carlos, Rute A. Sá Ferreira, Lucinda Reis, Per Jacobsson *Urethane cross-linked poly(oxyethylene)/siliceous nanohybrids doped with Eu3+ ions.* Physical Chemistry Chemistry Physics, 2004. **6**: p. 638-648.

69.   A. Wendsjo, J.L., J, O. Thomas, G. C. Farrington, *The effect of temperature and concentration on the local environment in the system M(CF3SO3)2PEOn for M=Ni, Zn and Pb* Solid State Ionics, 1992. **53-56**: p. 1077-1082.

70.   M. Kakihana, S.S., L. M. Torell, *Dissociated ions and ion-ion interactions in poly(ethylene oxide) based NaCF3SO3 complexes* Solid State Ionics, 1990: p. 641-644.

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

Table 1. Details of the synthetic procedure of the d-PCL(530)/siloxane$_n$KCF$_3$SO$_3$ biohybrids.

n = [C(C=O)(CH$_2$)O]/K$^+$ (mol mol^{-1})	mPCL(530) (g)	m(KCF$_3$SO$_3$) (g)	Si/K$^+$ (mol mol^{-1})	Si/K$^+$ (g g^{-1})
200	1.07	0.08	92.39	68.09
100	1.04	0.01	55.49	41.09
40	1.09	0.03	21.93	16.31
29	1.19	0.05	15.37	11.43
21	1.10	0.07	11.14	8.28
10	1.13	0.15	5.39	4.01
4	1.08	0.35	2.20	1.63
2	1.07	0.64	1.18	0.87
1	1.04	1.31	0.56	0.42
0.5	1.07	2.66	0.21	0.20

Table 2. Conductivity maxima of d-PCL(530)/siloxane$_n$M(CF$_3$SO$_3$)$_m$ biohybrids.

M	Ionic Conductivity (S cm^{-1})			Reference
	T = 35 ºC	T = 50 ºC	T = 104 ºC	
Li$^+$(n = 0.5)	4x10^{-6}	1x10^{-6}	6.7x10^{-5}	[47]
Mg^{2+} (n = 34)	8x10^{-9}	3x10^{-8}	9x10^{-7}	[47]
Li$^+$/Eu^{3+} (n = 6.1)	3x10^{-6}	1x10^{-5}	1.6x10^{-4}	[48]
K$^+$ (n = 4)	1x10^{-7}	2x10^{-7}	2.5x10^{-6}	this work

Table 3. Average spectral transmittance (ΔT) and optical density (ΔOD) exhibited by ECDs incorporating the d-PCL(530)$_n$KCF$_3$SO$_3$ biohybrids

n	T (%)			ΔT(%)	ΔOD$_{\lambda = 555\ nm}$
	as-deposited	bleached	colored		
29	76.4	74.6	57.0	17.6	0.13
21	76.7	75.6	55.0	20.6	0.16
4	77.7	76.5	60.1	16.4	0.11